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(54) Title: A PROCESS FOR IMPROVING THE EFFECTIVENESS OF A PROCESS CATALYST

(57) Abstract

This invention relates to a process for improving the effectiveness of a refinery process catalyst. The process comprises treating the refinery process catalyst with an effective amount of reducing agent selected from the group consisting of hydrazine, oximes, hydroxylamines, carbohydrazide, erythorbic acid, and mixtures thereof.

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**A PROCESS FOR IMPROVING THE EFFECTIVENESS
OF A PROCESS CATALYST**

TECHNICAL FIELD

5 This invention relates to a process for improving the effectiveness of a process catalyst. The process comprises treating the process catalyst with a reducing agent selected from the group consisting of hydrazine, oximes, hydroxylamines, carbohydrazide, erythorbic acid, 10 and mixtures thereof.

BACKGROUND OF THE INVENTION

Catalytic reforming is used in the refining of crude oil to increase the yield of higher octane gasoline which 15 sells at higher prices. In catalytic reforming, the paraffins and naphthenes are passed through the reformer with the goal of minimizing cracking. Instead their structure is rearranged to form higher octane aromatics. Essentially catalytic reforming converts low octane 20 paraffins to naphthenes. Naphthenes are converted to higher octane aromatics. Aromatics are left essentially unchanged.

Refineries generally use a platinum catalyst or platinum alloy supported on a silica or silica-aluminum 25 substrate as the reforming catalyst, although other catalysts, including the oxides of aluminum, chromium, molybdenum, cobalt, and silicon can be used.

In the strong reducing environment and elevated temperatures (500°C to 600°C) of the reformer, the catalyst 30 becomes contaminated with metals, such as lead, iron, nickel, vanadium, sulfur compounds, arsenic, and coke. The result is that the catalyst becomes inactive and the efficiency of the reformer decreases. In order to reduce contamination of the reformer catalyst, most reformer 35 catalysts have a guard bed for the catalyst which removes contaminants from the feed stream. Over a period of time,

-2-

contaminants still break through to the reformer catalyst and reduce catalytic activity.

As the activity of the catalyst decreases, the reaction temperature of the reformer is increased to 5 maintain the desired output. Additionally, organic chloride containing compounds are fed to the reformer to reactivate the catalyst on a periodic basis or continuously at a low dosage. The activity of the reformer catalyst is a function of surface area, pore 10 volume, active platinum and organic chloride content. The efficiency of the reformer is reduced during operation by coke deposition, chloride loss, and contaminants such as sulfur, lead, heavy metals, and oxygen.

When the catalyst becomes depleted, it is necessary 15 to regenerate the catalyst. The activity of the catalyst can be restored by high temperature oxidation of the coke followed by chloriding. This regenerative process allows the reformer to operate for up to a 24 month period between regenerations. Normally the catalyst can be 20 regenerated at least three times before it has to be replaced and returned to the manufacturer for reclamation.

SUMMARY OF THE INVENTION

This invention relates to a process for improving the 25 effectiveness of a process catalyst which comprises:

treating said process catalyst with an effective amount of a reducing agent selected from the group consisting of hydrazine, oximes, hydroxylamines, carbohydrazide, erythorbic acid, and mixtures.

Indirect evidence and direct evidence indicates that 30 the treatment of the process catalyst by the subject process reduces or retards the formation of metal contaminants, oxygen, sulfur, and coke on the process catalyst. Thus the process could be alternatively

-3-

characterized as a process for reducing and/or retarding the contamination of a process catalyst.

Reducing or retarding the contamination of the process catalyst results in the increased effectiveness of the reformer. This is shown by yields across the reformer, higher octane gasoline, and less benzene in the reformate. Moreover, since yields of higher octane gasoline are increased, the refinery can blend lower grade fuels into the gasoline. Furthermore, the reformer can also be operated at lower temperature and pressure thus minimizing coking and cracking while making the same octane gasoline and improving yield. Finally, the refinery can save money and time spent on catalyst regeneration by increasing the life of the catalyst and the time between regenerations.

Process catalysts which benefit from this treatment include reforming, hydrotreating, hydrocracking, isomerization, hydrogenation, and guard bed catalysts. Treating the process catalyst involves adding the reducing agent to a process stream which will enable the reducing agent to come into contact with the process catalyst. Examples of process streams which will provide such contact between the reducing agent and the process catalyst include stripper steam, crude overhead, naphtha, splitter feed, refining feed, and feedlines for chloriding chemicals used in the reformer.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic diagram of a simple refinery.

30

DEFINITIONS AND ABBREVIATIONS

BZE -- benzene.

CCAT -- catalyst contamination after treatment.

CCBT -- catalyst contamination before treatment.

-4-

CYH -- cyclohexane.

DREWCOR -- DREWCOR is a registered trademark of Ashland Oil, Inc. DREWCOR 2130 corrosion inhibitor is chemically defined as a blend of amines and MEKOR such 5 that the amount of MEKOR is about 5 percent by weight.

FEED POINT -- place where reducing agent is injected into the sulfur containing hydrocarbon process stream.

REFINERY PROCESS CATALYST -- a refinery process catalyst is a catalyst used in refining crude oil, 10 particularly catalysts used in the reforming of gasoline.

REFINERY PROCESS STREAM -- any refinery stream which comes into contact with a refinery process catalyst, particularly hydrocarbon streams which flow through the reformer of the refinery and come into contact with the 15 reformer catalyst, most particularly three phase refinery process streams which carry a liquid hydrocarbon phase, a gaseous hydrocarbon phase, and an aqueous phase.

MCP -- methyl cyclopentane.

MEKOR -- MEKOR is a registered trademark of Ashland 20 Oil, Inc. and is chemically defined as methyl ethyl ketoxime [$\text{H}_3\text{C}(\text{C}=\text{NOH})\text{CH}_2\text{CH}_3$].

MOTOR OCTANE NUMBER (MON) -- motor octane number measured by ASTM D-357 and is a guide to engine performance at high speeds or under heavy load conditions.

25 PETROLEUM PRODUCTS -- products produced by refining crude oil including gasoline, diesel fuel, propane, jet fuel, kerosene, propane, naphtha, benzene, gasoline, aniline, etc.

ppm -- parts per million MEKOR.

30 REFORMATE -- reformed aromatics, primarily naphtha, which is upgraded in octane by means of catalytic reforming.

RESEARCH OCTANE NUMBER (RON) -- research octane number measured by ASTM D-2699. A standardized test

-5-

engine operating under standardized conditions (600 rpm) is used. Results are comparable to those obtained in an automobile engine operated at low speed.

SAMPLE POINT -- place where a sample of a treated hydrocarbon stream is taken to determine if there was a reduction in catalyst contaminants.

SUM C₆ -- sum of compounds having 6 carbon atoms.

10 $\frac{R + M}{2}$ = average of RON and MON.

YIELD -- a percentage calculated by subtracting the liquid weight of the product that comes out of the reformer from the liquid weight of the feed which goes into the reformer and then dividing by 100.

15

DETAILED DESCRIPTION OF DRAWING

FIG. 1 illustrates the flow chart of a simple refinery. It shows the sample points 1-12 for the process streams tested, feedpoints for MEKOR 21-27, storage tanks 31-34, reformers 41-44, vessels 51-61, boiler 71, and hydrogen flare 72. Raw untreated crude oil 31 is fed to the desalter 54 where it is desalted and pumped into the crude tower 51. From the crude tower, a crude gasoline fraction is pumped into the raw gas accumulator 53 and then to the splitter tower 55. Fractions of the separated gasoline are pumped from the splitter tower to the depropanizer 57, the reformer 41-44, and to the hydrogen separator 59. The fraction from the hydrogen separator is pumped to the stabilizer tower 60. MEKOR is fed into the process at feedpoints 21-27. Sample points include 1-12.

The specific components in Fig. 1 are identified as follows:

-6-

SAMPLE POINTS

- 1 RAW CRUDE
- 2 CRUDE OUT OF DESALTER
- 5 3 WATER OUT OF DESALTER
- 4 DIESEL TO STORAGE TANK
- 5 WATER OUT OF RAW GAS ACCUMULATOR
- 6 SPLITTER BOTTOMS
- 7 STABILIZER BOTTOMS
- 10 8 WATER OUT OF STABILIZER ACCUMULATOR
- 9 STABILIZER PROPANE
- 10 WATER OUT OF SPLITTER ACCUMULATOR
- 11 WATER OUT OF DEPROGANIZER ACCUMULATOR
- 12 DEPROGANIZER PROPANE

15

CHEMICAL FEED POINTS

- 21 MEKOR INTO RAW CRUDE
- 22 MEKOR INTO STRIPPING STEAM TO CRUDE TOWER
- 23 MEKOR INTO CRUDE TOWER REFLUX
- 20 24 DREWCOR 2130 INTO CRUDE TOWER REFLUX
- 25 MEKOR INTO SPLITTER TOWER FEED
- 26 1,1,1 TRICHLOROETHANE INTO REFORMATE FEED
- 27 MEKOR INTO REFORMERS

25

STORAGE TANKS

- 31 RAW CRUDE
- 32 DIESEL
- 33 GASOLINE
- 34 PROPANE

30

REFORMERS

- 41 REFORMER #1
- 42 REFORMER #2
- 43 REFORMER #3

-7-

44 REFORMER #4

VESSELS

- | | | |
|----|----|--------------------------|
| 5 | 51 | CRUDE TOWER |
| | 52 | DIESEL DRIER |
| | 53 | RAW GAS ACCUMULATOR |
| | 54 | DESALTER |
| | 55 | SPLITTER TOWER |
| 10 | 56 | SPLITTER ACCUMULATOR |
| | 57 | DEPROPANIZER TOWER |
| | 58 | DEPROPANIZER ACCUMULATOR |
| | 59 | HYDROGEN SEPARATOR |
| | 60 | STABILIZER TOWER |
| 15 | 61 | STABILIZER ACCUMULATOR |

OTHER

- | | | |
|----|----|----------------|
| | 71 | BOILER |
| 20 | 72 | HYDROGEN FLARE |

DETAILED DESCRIPTION OF THE INVENTION

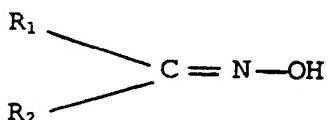
This process relates to improving the effectiveness of a refinery process catalyst. It is believed this improved effectiveness results because the treatment reduces and/or retards the contamination of the refinery process catalyst. Sources of catalyst contamination are metals, such as lead, iron, vanadium, and nickel, sulfur compounds, arsenic, and coke.

The reducing agents used in this process for improving the effectiveness a process catalyst are selected from the group consisting of hydrazine, oximes, hydroxylamines (such as N,N-diethylhydroxylamine),

-8-

erythorbic acid, and mixtures thereof. These reducing agents are described in U.S. Patents 5,213,678 and 4,350,606 which are hereby incorporated by reference. Preferably used as reducing agents are oximes such as the 5 ones described in U.S. Patent 5,213,678 as having the formula:

10



wherein R₁ and R₂ are the same or different and are selected from hydrogen, lower alkyl groups of 1-8 carbon atoms and aryl groups, and mixtures thereof. Most 15 preferably used as the oxime are aliphatic oximes, particularly methyl ethyl ketoxime.

An effective amount of reducing agent used to improve the effectiveness of the process catalyst will depend somewhat upon the specific result wanted: 20 improvement of the reformer yield, improved yield of high octane gasoline, reduced yield of benzene, reducing or retarding the contamination of the refiner. Actually, all these benefits are interrelated, and it is difficult to relate an effective amount of reducing agent to one of 25 these parameters, or state an exact amount of reducing agent which will relate to all benefits wanted. However, it can be stated in general that an effective amount will range from 5 ppm to 100 ppm of reducing agent based upon the catalyst feed stock, preferably from 50 ppm to 100 30 ppm. The catalyst feed stock typically consists of splitter bottoms, reformer feed, and process streams entering the reformer catalyst. Preferably the reducing agent is added to the process stream continuously.

-9-

The following detailed operating examples illustrate the practice of the invention in its most preferred form, thereby permitting a person of ordinary skill in the art to practice the invention. The 5 principles of this invention, its operating parameters, and other obvious modifications thereof will be understood in view of the following detailed examples.

EXAMPLES

10 The following examples will illustrate the use of MEKOR to improve the efficiency of a process catalyst used in the reformer of a refinery and the octane rating of the gasoline coming out of the reformer which is typically operated at temperatures of 500°C to 525°C and is under a 15 pressure of 200 to 300 psig. The process catalyst was a platinum catalyst arranged on a fixed bed. MEKOR was added to the reformer 41-44 to a pressurized naphtha feed line 25. The temperature of the naphtha feed line was about 250 °C to about 300°C.

20 The refinery used to test the effect of adding MEKOR to a process stream was a small refinery which refines approximately 10,000 barrels of crude oil per day. The diagram of the refinery is shown in Figure 1.

25

EXAMPLES

Control Examples C1-C3 in Table I show how the catalyst was working in the reformer before adding MEKOR.

Examples 1-2 in Table II show how the addition of 50 ppm MEKOR into the naphtha feed line 25 flowing to the 30 splitter tower 55 affected the effectiveness of the catalyst in terms of hours of operation and output.

-10-

TABLE I (Control)
(Reformer Length of Operation - Before MEKOR Addition)

Control Examples	Start of Run	End of Run	Hours of Operation	Throughput Bbls.
C1	6/21/93	7/27/93	936	66,292
C2	7/31/93	8/22/93	552	34,045
C3	8/28/93	10/5/93	960	64,227
Average			816	54,855

5

TABLE II
(Reformer Length of Operation - After MEKOR Addition)

Example	Start of Run	End of Run	Hours of Operation	Throughput Bbls.
1	10/8/93	1/11/94	2,304	149,125
2	1/16/94	3/26/94	1,668	100,238
3 Average			1,986	124,681

10

A comparison of the data in Tables I and II clearly shows that the addition of MEKOR to the reformer more than doubles the hours of operation and barrels of throughput when MEKOR is added to the naphtha process stream feeding the reformer and comes into contact with the reformer process catalyst.

15

A sample of the reformatte leaving the reformer before and after the treatment is measured for octane rating, benzene, and aniline. Table III, IV, and V show how the reformer was operating relative to these outputs before MEKOR was introduced into the reformer. Table IV shows how the reformer operated after adding 75 ppm of MEKOR to the naphtha stream (feedpoint 25) flowing to the reformer.

20

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-11-

TABLE III (Control)
Reformer Catalyst Performance Data
Before MEKOR Addition

Example	Reformer Feed(bpd)	Hours Into Run	Bbls. Thruput Since Startup	Octane R+M 2	Aniline	Yield %
C4	1750	168	9837	93.90	-15	77.99
C5	1715	192	11670	93.80	-14	78.57
C6	1647	216	13429	93.50	-11	79.06
C7	1571	240	15108	93.50	-10	79.72
C8	1469	264	16677	93.60	-14	81.09
Avg.	1630			93.66	-12	79.29

5

Table IV
 10 (Reformer Catalyst Performance Data - After MEKOR
 Addition)

Example	Reformer Feed (bpd)	Hours Into Run	Bbls. Thruput Since Startup	Octane R+M 2	Aniline	Yield %
3	1550	132	8884	93.00	-12	91.24
4	1550	156	10541	93.00	-10	89.75
5	1335	180	11968	97.00	-25	91.99
6	1606	252	17211	97.00	-20	86.55
7	1573	276	18891	97.00	-20	87.74
Avg.	1523			95.40	-17	89.45

Tables III and IV show the addition of MEKOR increases yield and octane number and decreases the
 15 aniline number.

-12-

Table V
Benzene Produced From Hydrocracking Reaction

Example	Hexane	MCP	CYH	BZE	Sum C6	BZE from Hydro-Cracking	MEKOR ppm
C10	2.337	0.367	0.030	9.245	9.642	2.508	0.0
10	2.462	1.010	0.045	7.120	8.175	1.041	20.0

5 Table V shows that the addition of MEKOR lowers the amount of benzene produced from the hydrocracking reaction. This is significant because future regulations by the Environmental Protection Agency will limit the amount of benzene in gasoline to less than one percent by 10 weight. Furthermore, if higher octane gasoline can be produced in a higher yield with less benzene, undesirable side reactions will be reduced.

-13-

CLAIMS

We claim:

1. A process for improving the effectiveness of a refinery process catalyst which comprises:
 - 5 treating said refinery process catalyst with an effective amount of a reducing compound selected from the group consisting of hydrazine, **oximes,** hydroxylamines, carbohydrazide, erythorbic acid, and mixtures thereof.
- 10
2. The process of claim 1 wherein said process catalyst is a catalyst used in the reformer of a refinery operation.
- 15
3. The process of claim 2 wherein the reducing agent is contacted with refinery process catalyst by feeding the reducing agent through a refinery process stream selected from the group consisting of stripper steam, crude overhead, naphtha, splitter feed, refining feed, and chloriding chemicals used in the reformer.
- 20
4. The process of claim 3 wherein the catalyst is a platinum catalyst.
- 25
5. The process of claim 4 wherein said reducing agent is an oxime.
- 30
6. The process of claim 5 wherein the amount of reducing agent used is from 5 ppm to 100 ppm based upon the weight of the catalyst feed stock.

-14-

7. The process of claim 6 wherein the oxime is fed into the naphtha stream.
8. The process of claim 7 wherein the oxime is methyl ethyl ketoxime and said methyl ethyl ketoxime is used in an amount of from 50 ppm to 100 ppm based upon the weight of the catalyst feedstock.
5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/06717

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :B01J 38/52, 38/04, 20/34
US CL : 502/27, 55, 20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 502/27, 55, 20; 208/140

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Please See Extra Sheet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category ^a	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,101,444 (BURK ET AL) 18 July 1978, claim 9.	1-8
Y	US,A, 4,190,554 (YAMAUCHI ET AL) 26 February 1980, col. 15, table 3.	1-8
Y	US,A, 3,879,311 (SCHOTT ET AL) 22 April 1975, col. 3, lines 1-10, col. 4, lines 60-66.	1-8
Y	US, A, 5,282,957 (WRIGHT ET AL) 01 February 1994, abstract.	1-8
Y	US,A, 5,100,532 (ROLING ET AL) 31 March 1992, abstract, col. 1, lines 30-56.	1-8
Y	US.A, 4,551,226 (FERN) 05 November 1985, abstract.	1-8

Further documents are listed in the continuation of Box C.

See patent family annex.

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Date of the actual completion of the international search

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Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

International application No.
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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A, 5,243,063 (DEVICARIS ET AL) 07 September 1993, abstract.	1-8
Y	US, A, 5,213,678 (RONDUM ET AL) 25 May 1993, abstract.	1-8

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/06717

B. FIELDS SEARCHED

Electronic data bases consulted (Name of data base and where practicable terms used):

APS

search terms: methyl ethyl ketoxime? catalyst? reactivat? regenerat? restor? activity rehabilitat? decontaminat? remov?
contaminant? hydrazine? carbohydrazide? ethyboric? hydroxylamine?